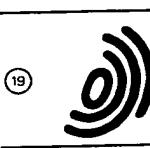


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PATENT ABSTRACTS OF JAPAN, vol. 9, no. 175 (C-292)[1898], 19th July 1985; & JP-A-60 47 053
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Description**BACKGROUND OF THE INVENTION**

5 This invention relates to an extrudable adhesive composition of ethylene copolymer and tackifying resin, useful for bonding structural polymers to barrier polymers.

Many attempts have been made to provide adhesive compositions which are particularly suitable for joining together layers of polymers, especially for joining structural polymers to polymers such as barrier resins. For example, Japanese Application 53 18653 discloses an adhesive resin for low temperature heat 10 sealing purposes comprising 3 to 100 parts by weight of a hydrogenated petroleum resin, and 100 parts by weight of an ethylene carboxylate-vinyl acetate copolymer obtained by copolymerizing an unsaturated carboxylic acid and/or anhydride with at least one vinylidene monomer in the presence of an ethylene-vinyl acetate copolymer.

Japanese application 60 51768 discloses a hot melt adhesive composition of 100 parts by weight of polymer component, 25 to 200 parts by weight of tackifier resin, and 75 parts by weight or less of wax. The polymer component comprises 25 to 75 weight % low crystallinity or amorphous ethylene alpha-olefin copolymer (20 to 50 mole % ethylene, 50 to 80 mole % alpha-olefin) and 25 to 75 weight % ethylene vinyl ester copolymer. Either polymer, or both, are modified with unsaturated carboxylic acid or its acid anhydride. The tackifier resin is a terpene resin or petroleum resin. The wax is a paraffin, microcrystalline 20 polyethylene, etc. The composition has a viscosity of 50 Pa.sec or less at 180 °C.

Japanese Application 01 27923 discloses a laminate in which a resin layer is coextrusion laminated onto an oriented film or Al foil. The adhesive is made of 50 to 99 weight percent ethylene-alpha-olefin random copolymer partially graft-modified with acid, and 1 to 50 weight percent tackifier. The ethylene-alpha-olefin copolymer has a density of 0.850 to 0.900 g/cc.

25 U.S. Patent 4,670,349 discloses an adhesive resin composition comprising 100 parts of an ethylene/vinyl acetate or ethylene/alpha-olefin random copolymer, 1-50 parts of modified polyethylene containing 0.01 to 10% grafted acid or derivative, and 1-125 parts hydrogenated aromatic petroleum resin. The resin composition is useful as an adhesive for polystyrene and ethylene vinyl alcohol copolymer.

U.S. Patent 4,337,297 discloses blends of a low density ethylene polymer and a copolymer of 70-90 % 30 ethylene with the balance acrylic or methacrylic acid or vinyl acetate, the two ethylene polymers comprising together 100 parts; an ionomer resin having an acid content of 1-10%, 2-100 parts; and optionally a tackifying resin, 0-150 parts. The blend is a useful adhesive for PET film.

U.S. Patent 4,367,113, Karim et al. discloses a similar blend except the low density polymer is replaced by an ethylene-alpha olefin copolymer or isotactic propylene polymer.

35 U.S. Patent 4,358,557 discloses a hot-melt adhesive comprising ethylene vinyl acetate copolymer, a tackifier resin selected from hydrocarbon resin, polyterpene resin or rosin ester, a paraffin wax and an aromatic hydrocarbon resin.

U.S. Patent 4,861,676 discloses a blend of ethylene copolymer, ethylene copolymer modified by grafting with a comonomer containing pendant acid or acid derivative functionality, styrene polymer, and 40 alicyclic resin modifier or stabilized rosin ester. The composition provides a useful adhesive, particularly for bonding polystyrene to barrier polymers.

U.S. Patent 4,861,677 discloses a blend of ethylene vinyl acetate copolymer, ethylene vinyl acetate copolymer modified by grafting with a comonomer containing pendant acid or acid derivative functionality, and impact-modified polystyrene. The composition provides a useful adhesive, particularly for bonding 45 polystyrene to gas barrier polymers.

SUMMARY OF THE INVENTION

The present invention provides an extrudable bonding resin composition consisting essentially of:

50 (a) about 65 to about 99 percent by weight of an ethylene copolymer portion consisting essentially of (i) about 1 to 100 percent by weight of a copolymer of about 50 to about 80 weight percent ethylene and 20 to about 50 weight percent of at least one comonomer copolymerized therewith selected from the group consisting of unsaturated mono- or dicarboxylic acids of 2-20 carbon atoms, esters or salts of said unsaturated mono- or dicarboxylic acids, vinyl esters of saturated carboxylic acids where the acid group has 1-18 carbon atoms, and optionally carbon monoxide, the carbon monoxide being present in an amount of 0 to about 30 weight percent; having grafted thereon side chains at least one comonomer unit in length, the comonomer units in said side chains being selected from the group consisting of ethylenically unsaturated mono-, di-, or polycarboxylic acids, ethylenically unsaturated

carboxylic acid anhydrides, metal salts and half-esters of such acids and anhydrides, and mixtures thereof, wherein the amount of said grafted comonomer units comprises about 0.03 to about 10 percent by weight of the total bonding resin composition, and

5 (ii) 0 to about 99 percent by weight of at least one copolymer of about 50 to about 80 weight percent ethylene and 20 to about 50 weight percent of at least one comonomer copolymerized therewith selected from the group consisting of unsaturated mono- or dicarboxylic acids of 2-20 carbon atoms, esters or salts of said unsaturated mono- or dicarboxylic acids, vinyl esters of saturated carboxylic acids where the acid group has 1-18 carbon atoms, and optionally carbon monoxide, the carbon monoxide being present in an amount of 0 to about 30 weight percent,

10 wherein the copolymer of (i) and each copolymer of (ii) contain at least one said copolymerized comonomer in common, the amount of each such common comonomer in each copolymer of (ii) being within about 10% of the amount of the corresponding comonomer in copolymer (i), and the total amount of said copolymerized comonomers other than such common comonomers in any such copolymer being less than about 10%; and

15 (b) about 1 to about 35 percent by weight of a tackifying resin.

The invention further provides a multiple layer structure comprising at least one structural layer, at least one barrier layer, and at least one bonding layer of the above extrudable bonding resin composition.

DETAILED DESCRIPTION OF THE INVENTION

20 The extrudable bonding resin of the present invention comprises a blend of about 65 to about 99 percent by weight, preferably about 80 to about 95 percent by weight, of an ethylene copolymer component, and about 1 to about 35 weight percent of a tackifying resin. The ethylene copolymer component comprises an ethylene copolymer grafted with pendant acid or certain acid derivative functionality. This grafted copolymer may be blended, if desired, with additional ungrafted ethylene copolymer. Such blending may be desirable in order to minimize the amount of the relatively more expensive grafted material, while maintaining the excellent adhesive properties of the composition.

25 The grafted ethylene copolymer is present in amounts of about 1 to about 100, and preferably about 5 to about 50 percent by weight of the ethylene copolymer portion of the composition. This component is a copolymer containing about 20 to about 50, and preferably about 25 to about 30 weight percent copolymerized comonomer selected from the group consisting of unsaturated mono- or dicarboxylic acids of 2-20 carbon atoms, esters or salts of said unsaturated mono- or dicarboxylic acids, vinyl esters of saturated carboxylic acids where the acid group has 1-18 carbon atoms, and carbon monoxide, the carbon monoxide being present in an amount of 0 to about 30 weight percent. (The amount of carbon monoxide is limited only because it is believed that preparation of polymers containing more than about 30 weight percent carbon monoxide is not feasible due to problems of reactor fouling.) Vinyl acetate is a preferred comonomer, but methyl acrylate, n-butyl acrylate, and the like, optionally with carbon monoxide present as a third monomer, are also quite suitable. The balance of the copolymer is substantially copolymerized with ethylene. Such copolymers are prepared by the well-known addition polymerization processes. Onto this copolymer are grafted additional comonomer units of carboxylic acid or certain carboxylic acid derivative functionality to form short sidechains. (It is believed that when maleic anhydride is the graft comonomer, the sidechains are only one or at most two monomer units long.) The melt index of the resulting graft copolymer, as measured by ASTM D1238 Condition "E", should be about 0.5 to about 40. Outside of these ranges, processing becomes more difficult, and flow instabilities may result.

30 45 The grafting monomer is selected from the group consisting of ethylenically unsaturated mono-, di-, or polycarboxylic acids, ethylenically unsaturated carboxylic acid anhydrides, and metal salts and half-esters of such acids and anhydrides. Examples of the acids and anhydrides include acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, crotonic acid, itaconic anhydride, maleic anhydride, and dimethyl maleic anhydride, and salts and half-esters thereof. Among the acids and anhydrides that are particularly useful are maleic anhydride and maleic acid.

50 55 The method for grafting of the comonomer onto the ethylene copolymer can be any of the processes which are well known in the art. For example, grafting can be carried out in the melt without a solvent, as disclosed in European Patent Application 0 266 994, incorporated herein by reference, or in solution or dispersion. Melt grafting can be done using a heated extruder, a Brabender™ or Banbury™ mixer or other internal mixers or kneading machines, roll mills, and the like. The grafting may be carried out in the presence of a radical initiator such as a suitable organic peroxide, organic perester, or organic hydroperoxide. The graft copolymers are recovered by any method which separates or utilizes the graft polymer that is formed. Thus the graft copolymer can be recovered in the form of precipitated fluff, pellets, powders, and

the like.

The amount of monomer grafted onto the ethylene copolymer is not particularly limiting, and may be as low as about 0.03 weight percent or as much as about 5 percent or even 10 percent, based on the weight of the grafted ethylene copolymer. The total amount of graft polymer in the total adhesive composition, 5 however, is important, and should be between about 0.03 and about 10 weight percent of the total composition, in order to obtain superior adhesive and bonding properties.

The ungrafted ethylene copolymer component comprises at least one comonomer similar to that described above, but without the grafted comonomer. In order to achieve good peel strength in laminates prepared from the present adhesive, the comonomer of the ungrafted copolymer should be of a type and 10 amount sufficiently similar to that of the grafted copolymer that the grafted and ungrafted copolymers have a suitable degree of compatibility. Such copolymers are normally compatible if they contain the same or closely chemically related monomers (except for the graft comonomer) and the amounts of such monomers in the two copolymers are similar. Specifically, the grafted copolymer and each of the ungrafted copolymers (if there is more than one) should contain at least one said copolymerized comonomer in common and the 15 amount of each such common comonomer in the grafted copolymer and the ungrafted copolymer should be within about 10%, and preferably within about 5%, of each other. Thus if the grafted copolymer is based on an ethylene polymer containing 30 weight % n-butyl acrylate, the ungrafted copolymer should contain between about 20 and about 40 weight percent n-butyl acrylate. Small amounts of additional comonomers may also be present in one or both copolymers, but in order to retain compatibility each copolymer should 20 contain less than about 10% by weight of such comonomers that are not common to the other copolymer. Alternatively, closely similar comonomers, such as n-butyl acrylate and i-butyl acrylate could be interchanged while retaining compatibility. It is preferred that the graft copolymer be the same as the ungrafted copolymer, except for the presence of the grafted monomers. The melt index of the ungrafted copolymer should be about 0.05 to about 40.

25 The ungrafted copolymer component can be a single polymer or it can be more than one polymer, provided that the comonomer content of each such polymer is as described above, i.e., the polymers are mutually compatible. It has been sometimes found to be desirable that the ungrafted copolymer component be a mixture of two polymers having identical comonomer contents but having differing melt indices. For example, one copolymer can have a melt index of about 6 and a second can have a melt index of 25 or 30 higher. The mixture of these polymers should have an overall melt index within the range of about 0.05 to about 40, as indicated. Use of such a mixture of copolymers provides ease in processability in, for example extrusion coating.

It is similarly to be understood that the use of more than one graft copolymer will fall within the scope of the present invention, provided that the general principles of polymeric compatibility set forth herein are 35 maintained.

The second major component of the present invention is a tackifying resin, which is present at about 1 to about 35 weight percent, preferably about 5 to about 20 weight percent of the composition. Suitable tackifying resins may be selected from the categories of:

- 40 (i) alicyclic or aliphatic hydrocarbon resins;
- (ii) aromatic hydrocarbon resins;
- (iii) rosin and rosin derivatives; and
- (iv) terpene resins, or mixtures thereof.

These tackifying resins will generally have a ring-and-ball softening temperature (ASTM E-2858T) of 0 to 150 °C, preferably about 75 to about 140 °C.

45 The tackifying resins employed in the present invention are well known products available from commercial sources. Rosin tackifiers are described in the Kirk Othmer Encyclopedia of Chemical Technology, Interscience Publishers, Second Edition, Volume 17, pages 475-509. They include naturally occurring resins and chemically modified rosin derivatives obtained by hydrogenation, dehydrogenation, isomerization, and the like. Rosin derivatives includes rosin esters and rosin acids. Rosin acids are typically derived 50 from tall oil and can be mixtures of so called abietic types and primary types. Rosin esters are formed by esterifying rosin acid with a di-, tri-, or tetra-hydroxy aliphatic alcohol such as ethylene glycol, propylene glycol, glycerine, or pentaerythritol. The terpene resins are generally prepared by the polymerization of terpene hydrocarbons in the presence of Friedel-Crafts catalysts at moderately low temperatures. Petroleum resins, under which are classed aliphatic, alicyclic, and aromatic hydrocarbon resins, are described in the 55 Kirk Othmer Encyclopedia of Chemical Technology, Interscience Publishers, Third Edition, Volume 12, page 852. They are generally prepared by polymerization of 4-10 carbon atom hydrocarbons by selected Friedel Crafts catalysts. Higher or lower hydrocarbons may also be present. The product may be further partially or fully hydrogenated. Suitable aromatic resins can be prepared from polymerization of alpha methyl styrene,

vinyl toluene, and/or indene monomers.

In addition to the above mentioned components, the adhesive resin may contain small amounts of other materials commonly used and known in the art, such as antioxidants, stabilizers, slip additives, and fillers. The adhesive resin composition is prepared by blending the above described components by any suitable means, such as melt blending, extruding, etc. Further details are provided in the Examples which follow.

The composition of the present invention provides excellent adhesion to polyester and copolyester resins, vinyl chloride polymers, polycarbonates, polyethylenes, ethylene copolymers, ionomers, polystyrene, ethylene vinyl alcohol copolymer, polyamides, and the like. It also shows good adhesion to substrates such as aluminum foil. The adhesive is particularly useful for extrusion or coextrusion laminating structural and barrier polymers on to substrates such as polyester film, including multiple layer structures comprising at least two structural layers and at least one barrier layer. The structural layers may be of the same material or can be of different materials, e.g. one layer polyester and a second layer ionomer or acid copolymer. The adhesive can be used without having to resort to use of a solvent-based primer to prepare the polymer film surface. The resulting composite structures are useful in packaging and other applications.

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Examples

Adhesive blends for the Examples shown in Table 1 were prepared by dry blending the ingredients in a polyethylene bag and subsequently melt blending at 210 to 230 °C in a 28 or 53 mm Werner & Pfeiderer™ 20 twin screw extruder with a vacuum port. Each of the blends, listed in the Table, also contained about 0.10 weight percent Irganox™ 1010 hindered polyphenol stabilizer (not separately reported in the Table). For the extruded pellets, 0.3 weight percent Kemamide™ W20 was also added.

The adhesive properties of the blends were evaluated by measuring the peel strength of laminates prepared using a sheet of the adhesive between two layers of PET film. The layers of PET film were 12 25 micrometers (0.48 mils) thick; heat seal conditions were 210 °C, 0.8 seconds dwell time and 324 kPa (47 psig) applied pressure. Peel strength was measured by ASTM D 1876-72, modified in that the test was run at 305 mm/min, rather than 254 mm/min, and 3 to 6 duplicates of each sample were measured, rather than 10. The numbers are given as grams per 25 mm.

Comparative Examples C1 through C8 show poor peel strength because the acid polymer, which 30 contains 0% vinyl acetate comonomer, is used with a base resin containing 28% vinyl acetate. This is greater than the 10% difference in comonomer content between the ethylene polymer and its acid-modified ethylene polymer permitted in the present invention. In contrast, Examples 1 through 4 show good results because the difference in comonomer content between the acid polymer and the base resin is less than 10%.

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TABLE III^a

Ex.	E Copol. Type	High m.i. Copolymer Type	Acid Copol. Type	%	Tackifier Type	%	Adhesive Thickness micrometers	g Man in blend	Peel str. g/25mm
C9	E/28VA 85	(none)	(none)		P115	15	31	0	44.5
C10	" 70	"	E/10iBA/10MAA	15	P115	15	20	0	51.6
5	" 80	"	E/28VA-g-1.5MAN	5	P115	15	31	0.075	229.8
6	" 65	"	"	20	P90	15	18	0.3	122.6
7	" 65	"	"	20	P125	15	20	0.3	161.2
8	" 65	"	"	20	P140	15	23	0.3	190.7
9	" 65	"	"	20	F-105	15	20	0.3	133.9
10	" 65	"	"	20	R3102	15	25	0.3	165.7
11	" 65	"	"	20	R6108	15	25	0.3	172.5
12	" 65	"	"	20	R1126	15	25	0.3	178.2
13	" 65	"	"	20	M115	15	25	0.3	158.9
14	" 65	"	"	20	M135	15	30	0.3	193.0
15	" 55	E/28VA ^b 10	"	20	P115	15	25	0.3	178.1
C11	" 60	" 20	"	20	(none)	0	23	0.3	179.3
16	" 45	" 20	"	20	P115	15	30	0.3	238.2
17	" 45	" 20	"	20	F-105	15	18	0.3	153.2

^a Additional materials not identified in Table I: E/28VA^b, in the second column, is identical to the first E/28VA except that its melt index is 25 dg/min. P125 is Arkon^b 100% hydrogenated C₉ hydrocarbon resin, R&B 125°C. P120 is a comparable material, R&B 140°C. P140 is Arkon^b 100% hydrogenated C₉ hydrocarbon resin, R&B 115°C. M115 is Arkon^b M115 85% hydrogenated C₉ hydrocarbon resin, R&B 135°C. M135 is a comparable material, R&B 135°C. F-105 is Floral^b 105 65% hydrogenated resin ester from Hercules, R&B 104°C. R3102 is Regalrez^b 3102, 30% hydrogenated hydrocarbon resin from Hercules, R&B 102°C. R6108, a comparable resin, is 60% hydrogenated, R&B 108°C. R1126 is 100% hydrogenated, R&B 126°C.

Ex.	E Copol. Type	High m.i. Copolymer			Tackifier Type	Adhesive Thickness micrometers	% MAN in blend	Peel Str. g/25mm
		Type	%	Type				
C12	(none)	(none)		E/10IBA/10MMA	100 (none)	36	0	227
C13	E/28VA	50	E/28VA	15	EPDM-g-2MAN	15	33	0.4
C14	"	50	"	15	E/9VA-g-1.5MAN	20	"	894
C15	E/9VA	65	(none)	"	20	"	41	0.3
18	E/28VA	35	E/28VA	30	E/28VA-g-1.5MAN	20	"	477
19	"	15	"	50	"	15	38	0.3
20	"	45	E/28VA	20	"	15	33	513
21	E/20MA	65	(none)	E/20MA-g-1.5MAN	20	"	33	1285
C16	(none)	"	"	E/21MA/4EHM	85	"	38	0.3
22	E/30nBA/10CO	75	"	E/nBA/CO-g-MAN	10	"	51	1407
23	"	75	"	"	10	F-105	15	1476

a. Additional materials not identified in previous Tables:

EPDM-g-2MAN - ethylene propylene diene rubber grafted with 2% maleic anhydride
 E/9VA - ethylene/9% vinyl acetate copolymer, melt index 7
 E/9VA-g-1.5MAN - ethylene/9% vinyl acetate copolymer, melt index 1.2, grafted
 with 1.5 weight percent maleic anhydride
 E/28VA - ethylene/28% vinyl acetate copolymer, melt index 43
 E/20MA - ethylene/20% methyl acrylate copolymer, melt index 2
 E/20MA-g-1.5MAN - ethylene/20% methyl acrylate copolymer, melt index 3.6,
 grafted with 1.5 weight percent maleic anhydride
 E/21MA/4EHM - ethylene/21% methyl acrylate/4% ethyl hydrogen maleate terpolymer
 E/30nBA/10CO - ethylene/30% n-butyl acrylate/10% co terpolymer, melt index 5
 E/nBA/CO-g-MAN - ethylene/30% n-butyl acrylate/10% co terpolymer, melt
 index 4.7, grafted with 0.3 weight percent maleic anhydride

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In Table 4, the multiple layer structures were made by coextrusion coating a layer of ionomer (ethylene
 55 methacrylic acid copolymer containing 15% methacrylic acid moieties, melt index 10 dg/min, 22%
 neutralized with zinc ions), 23 micrometers thick, and a layer of adhesive onto corona-treated PET film, 12
 micrometers thick. The adhesive blends were melted in a 63 mm extruder with barrel temperatures from
 154°C at the rear to 232°C at the front. The ionomer resin was melted in a 114 mm extruder with barrel

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temperatures from 177°C in the rear to 232°C at the front. Both melt streams were fed into a 107 cm (42 inch) die set at 232°C. The air gap was set at 16.5 centimeters. Line speed was 122 meters per minute.

Comparative Examples C17, C18, C22, C24 and C25 give poor results because the difference in vinyl ester comonomer content between the acid-containing polymer and the base polymer is greater than 10%.

5 Comparative Example C19 compares unfavorably with Example 28 because it contains no tackifier. In Comparative Example C20, the acrylate comonomer content of the ethylene polymer is below 20 weight percent. Comparative Examples C21, C23 and C26 contain no acid polymers.

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TABLE IV

Ex.	E Copol. ^b	High m.i. Copol. ^c	Acid Copol. Type	Tackifier Type	Adhesive Thickness μm	MAN		Peel Str., g/25mm green	Peel Str., g/25mm 1 wk	Peel Str., g/25mm 4 wk
						in blend	green			
C17	46	E/15MAA ^a	8	(none)	18	0	423	319	454	
C18	89	0	E/10iBA/10MAA	20	"	10.2	0	347	245	293
C19	99	0	E/28VA-g-1.5MAN	10	"	8	0.15	276	416	---
C20	9	0	E/10iBA/10MAA	100	"	9	0	133	142	---
C21	95	0	(none)	0	F-105	5	23	0	428	251
C22	75	0	E/10iBA/10MAA	20	P115	5	28	0	414	378
24	55	0	E/28VA-g-1.5MAN	40	R6108	5	20	0.60	450	717
25	60	15	"	"	"	5	20	0.30	512	698
26	40	15	"	30	P125	5	23	0.45	563	681
C23	80	15	(none)	0	R3102	5	18	0	470	456
C24	60	15	E/10iBA/10MAA	10	P90	15	15	0	510	454
C25	50	15	"	20	F-105	15	15	0	731	408
27	30	15	E/28VA-g-1.5MAN	40	P115	15	10	0.60	557	744
C26	85	0	(none)	0	R6108	15	18	0	583	559
C27	65	0	E/10iBA/10MAA	20	P90	15	10	0	509	394
28	55	0	E/28VA-g-1.5MAN	20	R3102	15	8	0.30	580	787
29	45	0	"	40	P125	15	10	0.60	590	792
30	45	0	"	40	"	15	8	0.60	583	607
										838

a. Ethylene/15 wt.% methacrylic acid copolymer, melt index 10.

b. In each case the polymer was E/28VA, melt index 6.

c. In each case the polymer was E/28VA, melt index 25.

d. "Green" refers to peel testing conducted as soon as the test sample was made. "1 wk" and "4 wk" refer to peel testing conducted 1 week and 4 weeks respectively after sample manufacture.

55 In Table 5, the multiple layer structures of Examples 31 and 32 were made by coextrusion coating a layer of ionomer (as described for the Examples of Table 4), adhesive, a layer of ethylene vinyl alcohol copolymer containing 44 mol % ethylene, melt index 16, and adhesive onto PET film as described for the Examples of Table 4. The adhesive blends were melted in a 63 mm extruder with barrel temperatures from 154°C at the rear to 232°C at the front. The ionomer resin was melted in a 114 mm extruder with barrel

temperatures from 177°C in the rear to 232°C at the front. The ethylene vinyl alcohol resin was melted in a 62.5 mm extruder with barrel temperatures from 177°C in the rear to 232°C at the front. The melt streams were fed into a feedblock in which the adhesive stream was split into two. The 1067 mm die was at 232°C. The air gap was set at 16.5 centimeters. Line speed was 122 meters per minute. Good adhesive strength is 5 achieved in the structure.

The multiple layer structures of Examples 33-39 were made with several different substrates. The adhesive blends were melted in a 87.5 mm extruder with barrel temperatures from 180°C in the rear to 240°C at the front. The ionomer and acid copolymer resins were melted in a 62.5 mm extruder with a similar temperature profile. The melt streams were fed into a die with a slot width of 800 mm. The die 10 was set at 240°C. The air gap was at 15 centimeters. Good bond strengths are obtained with different substrates.

The multiple layer structures of Examples 40-49 were prepared by coextrusion of an adhesive layer between a copolyester layer and an ethylene vinyl alcohol copolymer containing 30 mol% ethylene 15 moieties. The copolyester was a high melt viscosity copolyester of ethylene glycol copolymerized with about 86% terephthalic and about 14% isophthalic acid, further containing 0.4% comonomer moieties derived from trimellitic acid. The adhesive blends were melted at 160°C in a 25 mm extruder at 4-6 rpm. The copolyester was fed through a 37.5 mm extruder at 30-45 rpm at 240°C. The extrudate was cast onto chill rolls maintained at 60°C. The takeup speed of the sheet was 1.5 m/min. Good bonding is achieved to copolyester and ethylene vinyl alcohol copolymer with these compositions.

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55 **Claims**

1. An extrudable bonding resin composition consisting essentially of:

(a) 65 to 99 percent by weight of an ethylene copolymer portion consisting essentially of

TABLE V

Ex.	Ethylene Copol. ^a	High m.i. Copol. ^b	Acid copol. ^c	copol. ^c	tackifier	Type	Thickness μ	Adhesive in blend		Peel str., g/25mm green 1 wk	Peel str., g/25mm 6 wk	Structure ^e PET/A/EVOH1/A/IONOMER1
								15	7.6			
31	65	0	20	R3102			5.1	0.3	583	674	---	
32	65	0	20	R6108			5.1	0.3	574	686	---	
33	50	15	20	R3102			5	0.3	---	367	383	PET/A/IONOMER2
34	50	15	20	"			10	0.3	---	567	633	"
35	50	15	20	"			5	0.3	---	450	483	"
36	50	15	20	"			15	0.3	---	717	783	"
37	50	15	20	R6108			10	0.3	---	d	d	PET/A/PET
38	50	15	20	R3102			25	0.3	---	d	d	PET/A/AC/Al foil
39	50	15	20	"			5	0.3	---	d	d	"
40	50	15	20	P125			10	0.3	---	d	d	POLYESTER/A/EVOH2
41	45	0	40	"			15	0.3	---	d	d	"
42	40	15	40	"			5	0.6	---	d	d	"
43	50	15	20	R3102			5	0.6	---	d	d	"
44	65	0	20	"			10	0.3	---	d	d	"
45	30	15	40	"			15	0.3	---	d	d	"
46	50	15	20	R3108			60	0.3	---	d	d	"
47	60	15	20	"			5	0.3	---	d	d	"
48	65	0	20	"			15	0.3	---	d	d	"
49	55	0	40	"			15	0.6	---	d	d	"

a. E/28VA, mi 6 b. E/28VA, mi 25 c. E/28VA-g-1.5MAnh, mi 2. d. Could not separate.

e. Multilayer structures as indicated, where A = adhesive layer (from this Table);

PET = polyethylene terephthalate film, 12 micrometers, corona treated

IONOMER1 = ethylene/15% methacrylic acid copolymer, 22 μ zinc neutralized, 25 micrometers

IONOMER2 = ethylene/8.7% methacrylic acid copolymer, 18 μ zinc neutralized, MI = 16, 25 μ

AC = ethylene/9% acrylic acid copolymer, melt index 10, 25 micrometers

Al foil = aluminum foil, 20 micrometers thick.

EVOH1 = ethylene vinyl alcohol copolymer, 44 mol % ethylene, MI = 16, 8 micrometers

EVOH2 = ethylene vinyl alcohol copolymer, 30 mol % ethylene, MI = 3, 80-120 micrometers

POLYESTER = copolymer of isoo-, terephthalic, and trimellitic acids, 185-405 micrometers

(i) 1 to 100 percent by weight of a copolymer of 50 to 80 weight percent ethylene and 20 to 50 weight percent of at least one comonomer copolymerized therewith selected from the group consisting of unsaturated mono- or dicarboxylic acids of 2-20 carbon atoms, esters or salts of said unsaturated mono- or dicarboxylic acids, vinyl esters of saturated carboxylic acids where the acid group has 1-18 carbon atoms, and carbon monoxide, the carbon monoxide being present in an amount of 0 to 30 weight percent; having grafted thereon side chains at least one comonomer unit in length, the comonomer units in said side chains being selected from the group consisting of ethylenically unsaturated mono-, di-, or polycarboxylic acids, ethylenically unsaturated carboxylic acid anhydrides, metal salts and half-esters of such acids and anhydrides, and mixtures thereof, wherein the amount of said grafted comonomer units comprises 0.03 to 10 percent by weight of the total bonding resin composition, and

5 (ii) 0 to 99 percent by weight of at least one copolymer of 50 to 80 weight percent ethylene and 20 to 50 weight percent of at least one comonomer copolymerized therewith selected from the group consisting of unsaturated mono- or dicarboxylic acids of 2-20 carbon atoms, esters or salts of said unsaturated mono- or dicarboxylic acids, vinyl esters of saturated carboxylic acids where the acid group has 1-18 carbon atoms, and carbon monoxide, the carbon monoxide being present in an amount of 0 to 30 weight percent,

10 wherein the copolymer of (i) and each copolymer of (ii) contain at least one said copolymerized comonomer in common, the amount of each such common comonomer in each copolymer of (ii) being within 10% of the amount of the corresponding comonomer in copolymer (i), and the total amount of said copolymerized comonomers other than such common comonomers in any such copolymer being less than 10%; and

15 (b) 1 to 35 percent by weight of a tackifying resin.

20 25 2. The composition of claim 1 wherein the ethylene copolymer portion consists essentially of 5 to 50 weight percent graft copolymer of (i) and 95 to 50 weight percent of at least one copolymer of (ii).

30 3. The composition of claim 1 or 2 wherein the copolymer of (i) and each copolymer of (ii) contain the same copolymerized comonomers and each comonomer in each copolymer of (ii) is within 5% of the amount of the corresponding comonomer in copolymer (i).

35 4. The composition of claim 1, 2 or 3 wherein the amount of ethylene copolymer portion is 80 to 95 weight percent and amount of the tackifying resin is 5 to 20 weight percent.

40 5. The composition of any one of claims 1 to 4 wherein the amount of each copolymerized comonomer in each of the copolymers of (i) and copolymer of (ii) is 25 to 30 percent by weight.

45 6. The composition of any one of claims 1 to 5 wherein the copolymer of (i) exclusive of the grafted comonomer units and each copolymer of (ii) are selected from the group consisting of ethylene vinyl acetate copolymer, ethylene methyl acrylate copolymer, ethylene n-butyl acrylate copolymer, and ethylene n-butyl acrylate carbon monoxide copolymer.

50 7. The composition of any one of claims 1 to 6 wherein the at least one copolymer of (ii) comprises two copolymers which differ in melt index.

45 8. The composition of any one of claims 1 to 7 wherein the grafted comonomer units are grafted onto polymer (i) in an amount of 0.05 to 5 weight percent of polymer (i).

55 9. The composition of claim 8 wherein the grafted comonomer units are ethylenically unsaturated mono, di, or polycarboxylic acids, anhydrides, or salts.

10. The composition of claim 9 wherein the anhydride is maleic anhydride.

11. The composition of any one of claims 1 to 10 wherein the tackifying resin has a ring and ball softening point of 0 to 150 °C and is at least one of the resins selected from the group consisting of:

55 (i) alicyclic or aliphatic hydrocarbon resins;

(ii) aromatic hydrocarbon resins;

(iii) rosin and rosin derivatives; and

(iv) terpene resins.

12. A multiple layer structure comprising at least one structural layer, at least one barrier layer, and at least one bonding layer of an extrudable bonding resin composition consisting essentially of

5 (a) 65 to 99 percent by weight of an ethylene copolymer portion consisting essentially of
 (i) 1 to 100 percent by weight of a copolymer of 50 to 80 weight percent ethylene and 20 to 50 weight percent of at least one comonomer copolymerized therewith selected from the group consisting of unsaturated mono- or dicarboxylic acids of 2-20 carbon atoms, esters or salts of said unsaturated mono- or dicarboxylic acids, vinyl esters of saturated carboxylic acids where the acid group has 1-18 carbon atoms, and carbon monoxide, the carbon monoxide being present in an amount of 0 to 30 weight percent; and grafted comonomer units of pendant ethylenically unsaturated mono-, di-, or polycarboxylic acids, ethylenically unsaturated carboxylic acid anhydrides, or metal salts or half-esters of such acids or anhydrides, wherein the amount of said grafted comonomer units comprises 0.03 to 10 percent by weight of the total bonding resin composition, and

10 (ii) 0 to 99 percent by weight of at least one copolymer of 50 to 80 weight percent ethylene and 20 to 50 weight percent of at least one comonomer copolymerized therewith selected from the group consisting of unsaturated mono- or dicarboxylic acids of 2-20 carbon atoms, esters or salts of said unsaturated mono- or dicarboxylic acids, vinyl esters of saturated carboxylic acids where the acid group has 1-18 carbon atoms, and carbon monoxide, the carbon monoxide being present in an amount of 0 to 30 weight percent,

15 wherein the copolymer of (i) and each copolymer of (ii) contain at least one said copolymerized comonomer in common, the amount of each such common comonomer in each copolymer of (ii) being within 10% of the amount of the corresponding comonomer in copolymer (i), and the total amount of said copolymerized comonomers other than such common comonomers in any such copolymer being less than 10%; and

20 (b) 1 to 35 percent by weight of a tackifying resin.

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13. The multiple layer structure of claim 12 wherein the structural layer is polyester and the barrier layer is ethylene vinyl alcohol copolymer or aluminum.

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14. The multiple layer structure of claim 12 comprising at least two structural layers, and wherein one structural layer is prepared from ionomer resin or acid copolymer and one structural layer is prepared from polyester.

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Patentansprüche

1. Extrudierbare Harzbindemasse, bestehend im wesentlichen aus:

40 (a) 65 bis 99 Gew.-% eines Ethylenkopolymer-Anteils, bestehend im wesentlichen aus
 (i) 1 bis 100 Gew.-% eines Copolymeren von 50 bis 80 Gew.-% Ethylen und 20 bis 50 Gew.-% von wenigstens einem Comonomeren, das damit copolymerisiert ist, ausgewählt aus der Gruppe, bestehend aus ungesättigten Mono- oder Dicarbonsäuren mit 2 bis 20 Kohlenstoffatomen, Estern oder Salzen der genannten ungesättigten Mono- oder Dicarbonsäuren, Vinylestern von gesättigten Carbonsäuren, worin die Säuregruppe 1 bis 18 Kohlenstoffatome besitzt, und Kohlenmonoxid, wobei das Kohlenmonoxid in einer Menge von 0 bis 30 Gew.-% vorhanden ist, das darauf aufgepropfte Seitenketten, die wenigstens eine Comonomer-Einheit lang sind, aufweist, wobei die Comonomer-Einheiten in den genannten Seitenketten ausgewählt sind aus der Gruppe, bestehend aus ethylenisch ungesättigten Mono-, Di- oder Polycarbonsäuren, ethylenisch ungesättigten Carbonsäureanhydriden, Metallsalzen und Halbestern von solchen Säuren und Anhydriden und aus Gemischen davon, worin die Menge der genannten gepropften Comonomer-Einheiten 0,03 bis 10 Gew.-% der gesamten Harzbindemasse umfaßt, und

45 (ii) 0 bis 99 Gew.-% von wenigstens einem Copolymer und 50 bis 80 Gew.-% Ethylen und 20 bis 50 Gew.-% von wenigstens einem damit copolymerisierten Comonomer, ausgewählt aus der Gruppe, bestehend aus ungesättigten Mono- oder Dicarbonsäuren mit 2 bis 20 Kohlenstoffatomen, Estern oder Salzen der genannten ungesättigten Mono- oder Dicarbonsäuren, Vinylestern von gesättigten Carbonsäuren, worin die Säuregruppe 1 bis 18 Kohlenstoffatome besitzt, und Kohlenmonoxid, wobei das Kohlenmonoxid in einer Menge von 0 bis 30 Gew.-% vorhanden ist,

50 aus Gemischen davon, worin die Menge der genannten gepropften Comonomer-Einheiten 0,03 bis 10 Gew.-% der gesamten Harzbindemasse umfaßt, und

55 (ii) 0 bis 99 Gew.-% von wenigstens einem Copolymer und 50 bis 80 Gew.-% Ethylen und 20 bis 50 Gew.-% von wenigstens einem damit copolymerisierten Comonomer, ausgewählt aus der Gruppe, bestehend aus ungesättigten Mono- oder Dicarbonsäuren mit 2 bis 20 Kohlenstoffatomen, Estern oder Salzen der genannten ungesättigten Mono- oder Dicarbonsäuren, Vinylestern von gesättigten Carbonsäuren, worin die Säuregruppe 1 bis 18 Kohlenstoffatome besitzt, und Kohlenmonoxid, wobei das Kohlenmonoxid in einer Menge von 0 bis 30 Gew.-% vorhanden ist,

60 worin das Copolymer von (i) und jedes Copolymer von (ii) wenigstens ein genanntes copolymerisier-

tes Comonomer gemeinsam enthalten, wobei die Menge eines jeden solchen gemeinsamen Comonomeren in jedem Copolymer von (ii) im Bereich von 10 % der Menge des entsprechenden Comonomeren in Copolymer (i) liegt und die Gesamtmenge der genannten copolymerisierten Comonomeren, außer solchen gemeinsamen Comonomeren, in jedem solchen Copolymer weniger als 10 % beträgt, und

5 (b) 1 bis 35 Gew.-% eines klebrigmachenden Harzes.

2. Masse nach Anspruch 1, worin der Ethylen-copolymer-Anteil im wesentlichen aus 5 bis 50 Gew.-% Propfcopolymer von (i) und 95 bis 50 Gew.-% von wenigstens einem Copolymer von (ii) besteht,

10 3. Masse nach Anspruch 1 oder 2, worin das Copolymer von (i) und jedes Copolymer von (ii) dieselben copolymerisierten Comonomere enthalten und jedes Comonomer in jedem Copolymer von (ii) im Bereich von 5 % der Menge des entsprechenden Comonomeren in Copolymer (i) liegt.

15 4. Masse nach Anspruch 1, 2 oder 3, worin die Menge des Ethylen-copolymer-Anteils 80 bis 95 Gew.-% beträgt und die Menge des klebrigmachenden Harzes 5 bis 20 Gew.-% beträgt.

5. Masse nach einem der Ansprüche 1 bis 4, worin die Menge eines jeden copolymerisierten Comonomeren in jedem der Copolymeren von (i) und des Copolymeren von (ii) 25 bis 30 Gew.-% beträgt.

20 6. Masse nach einem der Ansprüche 1 bis 5, worin das Copolymer von (i), ausschließlich der gepropften Comonomer-Einheiten, und jedes Copolymer von (ii) ausgewählt sind aus der Gruppe, bestehend aus einem Ethylen-Vinylacetat-Copolymer, Ethylen-Methylacrylat-Copolymer, Ethylen-n-Butylacrylat-Copolymer und einem Ethylen-n-Butylacrylat-Kohlenmonoxid-Copolymer.

25 7. Masse nach einem der Ansprüche 1 bis 6, worin wenigstens ein Copolymer von (ii) zwei Copolymeren umfaßt, die sich im Schmelzindex unterscheiden.

30 8. Masse nach einem der Ansprüche 1 bis 7, worin die gepropften Comonomer-Einheiten auf Polymer (i) in einer Menge von 0,05 bis 5 Gew.-% von Polymer (i) gepropft sind.

9. Masse nach Anspruch 8, worin die gepropften Comonomer-Einheiten ethylenisch ungesättigte Mono-, Di- oder Polycarbonsäuren, Anhydride oder Salze sind.

35 10. Masse nach Anspruch 9, worin das Anhydrid Maleinsäureanhydrid ist.

11. Masse nach einem der Ansprüche 1 bis 10, worin das klebrigmachende Harz einen Ring- und Ball- Erweichungspunkt von 0 bis 150 °C besitzt und wenigstens eines der Harze ist, ausgewählt aus der Gruppe, bestehend aus:

40 (i) alicyclischen oder aliphatischen Kohlenwasserstoffharzen;

(ii) aromatischen Kohlenwasserstoffharzen;

(iii) Kolophonium und Kolophonium-Derivaten; und

(iv) Terpenharzen.

45 12. Mehrschichtige Struktur, umfassend wenigstens eine Strukturschicht, wenigstens eine Barriereforschicht und wenigstens eine Bindeschicht aus einer extrudierbaren Bindeharzmasse, bestehend im wesentlichen aus

(a) 65 bis 99 Gew.-% eines Ethylen-copolymer-Anteils, bestehend im wesentlichen aus

50 (i) 1 bis 100 Gew.-% eines Copolymeren von 50 bis 80 Gew.-% Ethylen und 20 bis 50 Gew.-% von wenigstens einem Comonomeren, das damit copolymerisiert ist, ausgewählt aus der Gruppe, bestehend aus ungesättigten Mono- oder Dicarbonsäuren mit 2 bis 20 Kohlenstoffatomen, Estern oder Salzen der genannten ungesättigten Mono- oder Dicarbonsäuren, Vinylestern von gesättigten Carbonsäuren, worin die Säuregruppe 1 bis 18 Kohlenstoffatome aufweist, und Kohlenmonoxid, wobei das Kohlenmonoxid in einer Menge von 0 bis 30 Gew.-% vorhanden ist, und gepropften Comonomer-Einheiten aus angehängten ethylenisch ungesättigten Mono-, Di- oder Polycarbonsäuren, ethylenisch ungesättigten Carbonsäureanhydriden oder Metallsalzen oder Halbestern von solchen Säuren oder Anhydriden, worin die Menge der genannten gepropften Comonomer-Einheiten 0,03 bis 10 Gew.-% der gesamten Harzbindemasse umfaßt, und

(ii) 0 bis 99 Gew.-% von wenigstens einem Copolymer aus 50 bis 80 Gew.-% Ethylen und 20 bis 50 Gew.-% von wenigstens einem damit copolymerisierten Comonomer, ausgewählt aus der Gruppe, bestehend aus ungesättigten Mono- oder Dicarbonsäuren mit 2 bis 20 Kohlenstoffatomen, Estern oder Salzen der genannten ungesättigten Mono- oder Dicarbonsäuren, Vinylestern von gesättigten Carbonsäuren, worin die Säuregruppe 1 bis 18 Kohlenstoffatome aufweist, und Kohlenmonoxid, wobei das Kohlenmonoxid in einer Menge von 0 bis 30 Gew.-% vorhanden ist, worin das Copolymer von (i) und jedes Copolymer von (ii) wenigstens eines der genannten copolymerisierten Comonomeren gemeinsam enthalten, wobei die Menge eines jeden solchen gemeinsamen Comonomeren in jedem Copolymer von (ii) im Bereich von 10 % der Menge des entsprechenden Comonomeren in Copolymer (i) liegt und die Gesamtmenge der genannten copolymerisierten Comonomeren, außer solchen gemeinsamen Comonomeren, in jedem derartigen Copolymer weniger als 10 % beträgt, und

(b) 1 bis 35 Gew.-% eines klebrigmachenden Harzes.

13. Mehrschichtenstruktur nach Anspruch 12, worin die Strukturschicht ein Polyester und die Barrierefachicht ein Ethylen-Vinylalkohol-Copolymer oder Aluminium ist.

14. Mehrschichtenstruktur nach Anspruch 12, umfassend wenigstens zwei Strukturschichten, worin eine Strukturschicht aus einem Ionomerharz oder einem sauren Copolymer und eine Strukturschicht aus Polyester hergestellt ist.

Revendications

1. Une composition de résine liante extrudable, constituée essentiellement de :

(a) 65 à 99 pour cent en poids d'un composant copolymère d'éthylène, constitué essentiellement de

(i) 1 à 100 pour cent en poids d'un copolymère de 50 à 80 pour cent en poids d'éthylène et 20 à 50 pour cent en poids d'au moins un comonomère copolymérisé avec lui qui est choisi dans le groupe formé par les acides mono- ou dicarboxyliques insaturés de 2 à 20 atomes de carbone, les esters ou sels desdits acides mono- ou dicarboxyliques insaturés, les esters de vinyle d'acides carboxyliques saturés où le groupement acide compte 1 à 18 atomes de carbone, et l'oxyde de carbone, l'oxyde de carbone étant présent en une proportion de 0 à 30 pour cent en poids ; sur lequel sont greffées des chaînes latérales ayant une longueur d'au moins un motif de comonomère, les motifs de comonomère desdites chaînes latérales étant choisis dans le groupe formé par les acides mono-, di- ou polycarboxyliques éthyléniquement insaturés, les anhydrides d'acides carboxyliques éthyléniquement insaturés, les sels métalliques et les hémi-esters de ces acides et anhydrides, et leurs mélanges, la quantité desdits motifs de comonomère greffé étant de 0,03 à 10 pour cent en poids de la composition de résine liante totale, et

(ii) 0 à 99 pour cent en poids d'au moins un copolymère de 50 à 80 pour cent en poids d'éthylène et 20 à 50 pour cent en poids d'au moins un comonomère copolymérisé avec lui qui est choisi dans le groupe formé par les acides mono- ou dicarboxyliques insaturés de 2 à 20 atomes de carbone, les esters ou sels desdits acides mono- ou dicarboxyliques insaturés, les esters de vinyle d'acides carboxyliques saturés où le groupement acide compte 1 à 18 atomes de carbone, et l'oxyde de carbone, l'oxyde de carbone étant présent en une proportion de 0 à 30 pour cent en poids,

dans lequel le copolymère de (i) et chaque copolymère de (ii) contiennent en commun au moins un comonomère copolymérisé **sudit, la proportion de chaque tel comonomère commun dans chaque copolymère de (ii) ne différant pas de plus de 10 % de la proportion du comonomère correspondant dans le copolymère (i), et la proportion totale desdits comonomères copolymérisés autres que de tels comonomères communs dans chacun de ces copolymères étant inférieure à 10 % ; et**

(b) 1 à 35 pour cent en poids d'une résine d'adhésivité.

2. La composition de la revendication 1, dans laquelle le composant copolymère d'éthylène est constitué essentiellement de 5 à 50 pour cent en poids de copolymère greffé de (i) et 95 à 50 pour cent en poids d'au moins un copolymère de (ii).

3. La composition de la revendication 1 ou 2, dans laquelle le copolymère de (i) et chaque copolymère de (ii) contiennent les mêmes comonomères copolymérisés et la proportion de chaque comonomère dans

chaque copolymère de (ii) ne diffère pas de plus de 5 % de la proportion du comonomère correspondant dans le copolymère (i).

4. La composition de la revendication 1, 2 ou 3, dans laquelle la quantité du composant copolymère d'éthylène est de 80 à 95 pour cent en poids et la quantité de la résine d'adhésivité est de 5 à 20 pour cent en poids.
5. La composition de l'une quelconque des revendications 1 à 4, dans laquelle la proportion de chaque comonomère copolymérisé dans chacun des copolymères de (i) et du copolymère de (ii) est de 25 à 10 30 pour cent en poids.
6. La composition de l'une quelconque des revendications 1 à 5, dans laquelle le copolymère de (i) à l'exclusion des motifs de comonomère greffé et chaque copolymère de (ii) sont choisis dans le groupe formé par un copolymère éthylène-acétate de vinyle, un copolymère éthylène-acrylate de méthyle, un copolymère éthylène-acrylate de *n*-butyle et un copolymère éthylène-acrylate de *n*-butyle-oxyde de carbone.
15. Le composition de l'une quelconque des revendications 1 à 6, dans laquelle ledit au moins un copolymère de (ii) comprend deux copolymères qui diffèrent par l'indice de fluidité à l'état fondu.
20. La composition de l'une quelconque des revendications 1 à 7, dans laquelle les motifs de comonomère greffé sont greffés sur le polymère (i) en une proportion de 0,05 à 5 pour cent en poids du polymère (i).
25. 9. La composition de la revendication 8, dans laquelle les motifs de comonomère greffé sont des acides, anhydrides ou sels mono-, di- ou polycarboxyliques éthyléniquement insaturés.
10. La composition de la revendication 9, dans laquelle l'anhydride est l'anhydride maléique.
30. 11. La composition de l'une quelconque des revendications 1 à 10, dans laquelle la résine d'adhésivité a un point de ramollissement de 0 à 150 °C par la méthode bille et anneau et est au moins l'une des résines choisies dans le groupe formé par :
 - (i) les résines hydrocarbonées alicycliques ou aliphatiques ;
 - (ii) les résines hydrocarbonées aromatiques ;
 35. (iii) la colophane et les dérivés de la colophane ; et
 - (iv) les résines terpéniques.
12. Une structure multicouche comprenant au moins une couche structurale, au moins une couche de barrière et au moins une couche de liaison formée d'une composition de résine liante extrudable constituée essentiellement de
 - (a) 65 à 99 pour cent en poids d'un composant copolymère d'éthylène, constitué essentiellement de
 - (i) 1 à 100 pour cent en poids d'un copolymère de 50 à 80 pour cent en poids d'éthylène et 20 à 50 pour cent en poids d'au moins un comonomère copolymérisé avec lui qui est choisi dans le groupe formé par les acides mono- ou dicarboxyliques insaturés de 2 à 20 atomes de carbone, les esters ou sels desdits acides mono- ou dicarboxyliques insaturés, les esters de vinyle d'acides carboxyliques saturés où le groupement acide compte 1 à 18 atomes de carbone, et l'oxyde de carbone, l'oxyde de carbone étant présent en une proportion de 0 à 30 pour cent en poids ; et de motifs de comonomère greffé formés par des acides mono-, di- ou polycarboxyliques éthyléniquement insaturés, des anhydrides d'acides carboxyliques éthyléniquement insaturés, ou des sels métalliques ou hémi-esters de ces acides et anhydrides, en situation latérale, la quantité desdits motifs de comonomère greffé représentant 0,03 à 10 pour cent en poids de la composition de résine liante totale, et
 - (ii) 0 à 99 pour cent en poids d'au moins un copolymère de 50 à 80 pour cent en poids d'éthylène et 20 à 50 pour cent en poids d'au moins un comonomère copolymérisé avec lui qui est choisi dans le groupe formé par les acides mono- ou dicarboxyliques insaturés de 2 à 20 atomes de carbone, les esters ou sels desdits acides mono- ou dicarboxyliques insaturés, les esters de vinyle d'acides carboxyliques saturés où le groupement acide compte 1 à 18 atomes de carbone, et l'oxyde de carbone, l'oxyde de carbone étant présent en une proportion de 0 à 30

pour cent en poids,

dans lequel le copolymère de (i) et chaque copolymère de (ii) contiennent en commun au moins un comonomère copolymérisé susdit, la proportion de chaque tel comonomère commun dans chaque copolymère de (ii) ne différant pas de plus de 10 % de la proportion du comonomère correspondant dans le copolymère (i), et la proportion totale desdits comonomères copolymérisés autres que de tels comonomères communs dans chacun de ces copolymères étant inférieure à 10 % ; et

(b) 1 à 35 pour cent en poids d'une résine d'adhésivité.

10 13. La structure multicouche de la revendication 12, dans laquelle la couche structurale est formée d'un polyester et la couche de barrière est formée d'un copolymère éthylène-alcool vinylique ou d'aluminium.

15 14. La structure multicouche de la revendication 12, comprenant au moins deux couches structurales, et dans laquelle une couche structurale est préparée à partir de résine ionomère ou de copolymère acide, et une couche structurale est préparée à partir de polyester.

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